



AFRL-AFOSR-JP-TR-2017-0077

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## Development of Li-S Battery With Improved Sulphur Utilization and Cyclic Stability

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12/04/2017  
Final Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory  
AF Office Of Scientific Research (AFOSR)/ IOA  
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<b>REPORT DOCUMENTATION PAGE</b>				Form Approved OMB No. 0704-0188	
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<b>1. REPORT DATE (DD-MM-YYYY)</b> 04-12-2017		<b>2. REPORT TYPE</b> Final		<b>3. DATES COVERED (From - To)</b> 16 Jun 2015 to 16 Jun 2017	
<b>4. TITLE AND SUBTITLE</b> Development of Li-S Battery With Improved Sulphur Utilization and Cyclic Stability				<b>5a. CONTRACT NUMBER</b>	
				<b>5b. GRANT NUMBER</b> FA2386-15-1-4071	
				<b>5c. PROGRAM ELEMENT NUMBER</b> 61102F	
<b>6. AUTHOR(S)</b> Sundara Ramaprabhu				<b>5d. PROJECT NUMBER</b>	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> INDIAN INSTITUTE OF TECHNOLOGY MADRAS SARDAR PATEL ROAD Chennai, 600036 IN				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>	
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> AOARD UNIT 45002 APO AP 96338-5002				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b> AFRL/AFOSR IOA	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b> AFRL-AFOSR-JP-TR-2017-0077	
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> A DISTRIBUTION UNLIMITED: PB Public Release					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> The PI met the objectives for the 2 year project. The aim of this study is to use partially exfoliated MWNT (PENTs), a few of the walls of MWNT are unraveled into microporous graphene sheets, in combined with sulphur as a cathode material along with Li foil coupled with the PENTs coated polypropylene as anode to accomplish the challenges due to the poor sulphur utilization and cyclic stability. There are 2 publications under preparation as a result of this project.					
<b>15. SUBJECT TERMS</b> Lithium-Sulphur, AOARD, Graphene					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>  SAR	<b>18. NUMBER OF PAGES</b> 13	<b>19a. NAME OF RESPONSIBLE PERSON</b> CHEN, JERMONT
<b>a. REPORT</b>  Unclassified	<b>b. ABSTRACT</b>  Unclassified	<b>c. THIS PAGE</b>  Unclassified			<b>19b. TELEPHONE NUMBER (Include area code)</b> 315-227-7007

**Project Title:-**

*Development of Li-S battery with improved sulphur utilization and cyclic stability*

**Objectives:-**

The aim of this study is to use partially exfoliated MWNT (PENTs), a few of the walls of MWNT are unraveled into microporous graphene sheets, in combined with sulphur as a cathode material along with *Li foil coupled with the PENTs coated polypropylene as anode* to accomplish the challenges due to the poor sulphur utilization and cyclic stability.

**Specific objectives:-**

*The details of the technical approach intended to be adopted in the execution of the project will be as follows:-*

**Milestone I**

- *Synthesis of partially exfoliated MWNT (PENTs)-S nanocomposites*
- *Characterization of partially exfoliated MWNT (PENTs)-S nanocomposites with XRD, Raman, SEM, AFM, TEM and HRTEM*
- *Development and testing of Li-S battery with PENTs-S cathode, PENTs coated polypropylene anode*
- *Investigation of energy density, and cyclic stability Li-S battery*

**Milestone II**

- *Studies of enhanced electrochemical performance and the enhanced cyclability of PENTs coated polypropylene as anode materials*
- *Optimization of Li-S battery with PENTs-S cathode, PENTs coated polypropylene anode for improved sulphur utilization with cyclic stability of about 100 cycles.*

**Deliverables:-**

*The technical know-how and the processing and methodology of PENTs-S cathode, PENTs coated polypropylene anode for high energy density, and good cyclic stability lithium ion battery.*

**Duration:-**

*2 years*

## PROJECT FINAL REPORT

### **Synthesis of Partially Exfoliated Carbon Nanotubes (PECNTs)**

PECNTs were synthesized in three steps. In the first step, multi-walled carbon nanotubes (CNTs) were synthesized by catalytic chemical vapor deposition (CCVD). Misch-metal based alloy hydride was used as a catalyst and acetylene gas as a carbon precursor. The catalyst was loaded in quartz boat inside a tubular furnace and argon gas was allowed to create an inert atmosphere. The decomposition of acetylene gas at 700 °C over the catalyst initiates the growth of CNTs<sup>1</sup>.

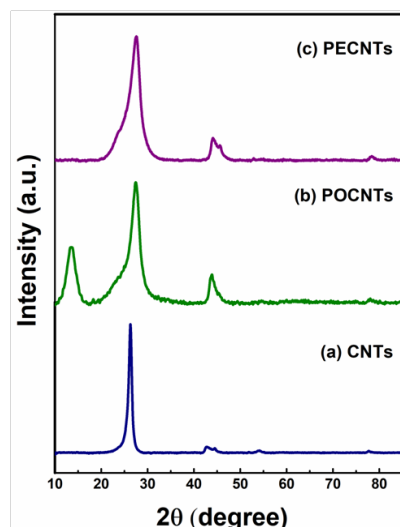
As grown CNTs consists of amorphous carbon and metal catalyst impurities, so as grown CNTs need to be purified. Purification of CNTs includes two steps. First, as grown CNTs were heated at 450 °C to remove carbonaceous impurities as well as to open ends of CNTs and secondly in order to remove metal catalyst these CNTs were refluxed with Conc. HNO<sub>3</sub> at 60 °C. Finally, acid-treated CNTs were washed with copious amount of deionized water and filtered and dried in vacuum at 60 °C for 12 h.

In the second step, purified CNTs were partially oxidized by modified Hummers method by maintaining CNTs to the KMnO<sub>4</sub> ratio as 1:1.5 g to get Partially Oxidized Carbon Nanotubes (POCNTs). POCNTs gained weight of about 60-70% due to the inclusion of functional groups in between the graphite layers of CNTs. In the third step, POCNTs were reduced by hydrogen gas in a tubular furnace to obtain Partially Exfoliation Carbon Nanotubes (PECNTs)<sup>2</sup>.

### **Synthesis of PECNTs sulfur (PECNTs/S) composite**

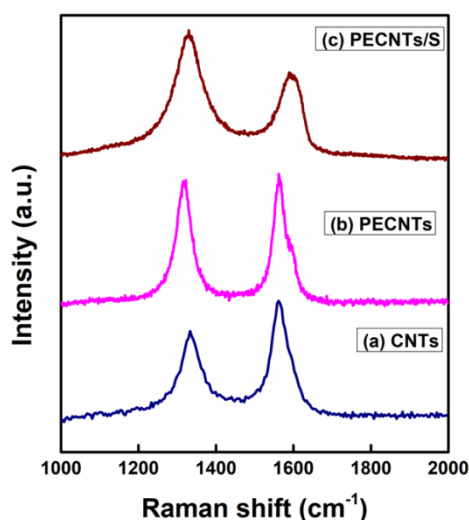
Sulfur was incorporated into PECNTs by melt diffusion method. In this CNTs to sublimed sulfur ratio was taken as 1:5 ground well and annealed at 155 °C for 12 h in argon atmosphere, final sample is labeled as PECNTs/S. A hydrophobic material was coated with polytetrafluoro ethylene (PTFE) coated carbon fiber by mixing polyvinylidene fluorodine binder with N-methyl-2-pyrrolidone.

## Material Characterization



**Fig.1. XRD pattern of (a) CNT (b) POCNT (c) PECNT**

Fig.1 shows XRD pattern of CNTs, POCNTs, PECNTs. In Fig. 1 (a), a sharp peak (002) at  $26.4^\circ$  corresponds to the crystalline nature of CNTs with an interlayer spacing 0.34 nm and (100) represents the graphitic carbon peak. In Fig. 1 (b) XRD peak of POCNTs (002) appears at  $10.5^\circ$  and  $26.4^\circ$ . In graphitic materials, due to the inclusion of functional groups, the interlayer spacing increases from 0.34 nm to 0.8 nm. The intensity of the peak  $10.4^\circ$  is less compared to the peak at  $26.4^\circ$  which signifies oxidation of very few outer layers of CNTs. Upon hydrogen exfoliation, all functional groups were removed as shown in Fig. 1(c) no peak at  $10.5^\circ$  and a strong intense peak at  $26.4^\circ$ .

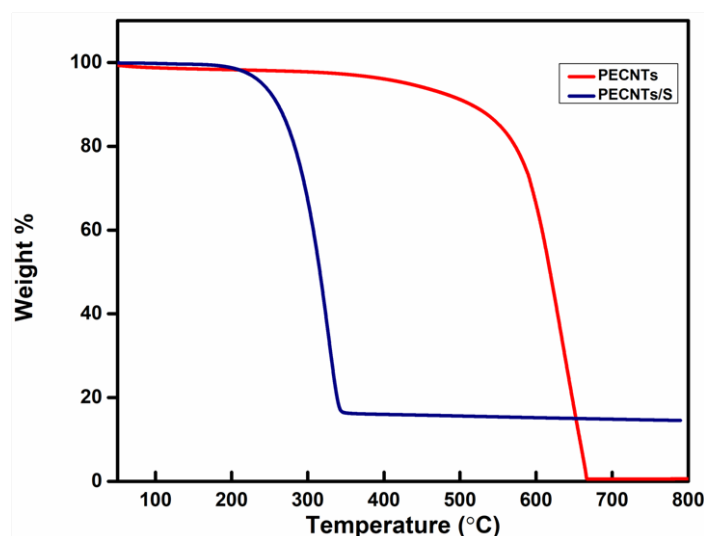


**Fig 2. Raman spectra of (a) CNTs (b) PECNTs (c) PECNTs/S**

**Table 1.  $I_D/I_G$  values of CNTs, PECNTs, PECNTs/S**

Sample	$I_D/I_G$
CNTs	0.84
PECNTs	1.02
PECNTs/S	1.25

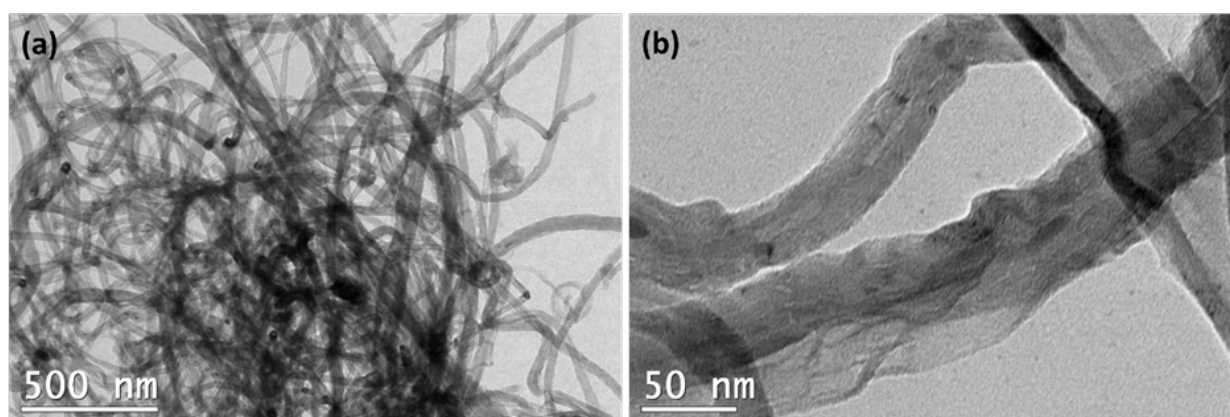
Raman spectra of CNT, PECNTs, PECNTs/S are shown in Fig.2. The peaks at  $1565\text{ cm}^{-1}$  and  $1335\text{ cm}^{-1}$  corresponds G band and D band of carbon respectively. The  $I_D/I_G$  ratio listed in table1 gives the purity of carbon nanotubes.



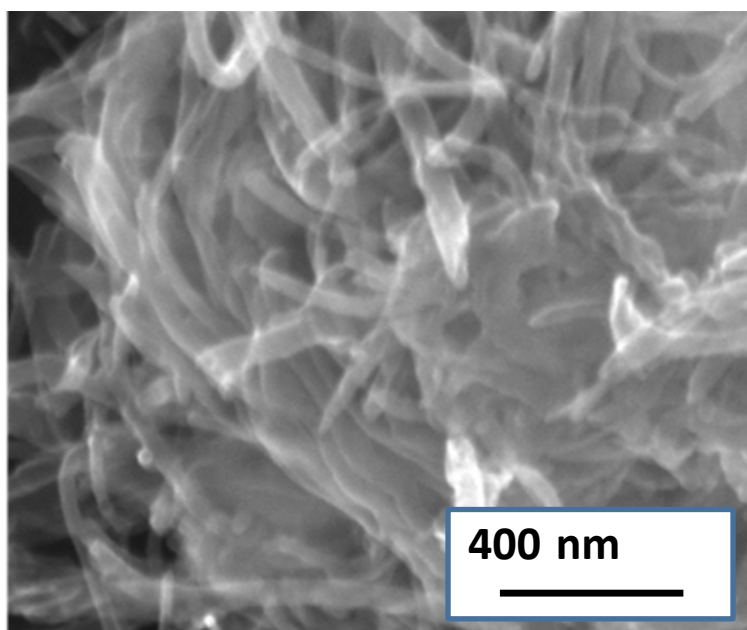
**Fig.3 TGA of PECNTs and PECNTs/S**

Thermogravimetric analysis has been carried out in air and argon atmosphere at a heating rate of  $20\text{ °C min}^{-1}$  for PECNTs and PECNTs/S respectively. TGA of PECNTs shown in Fig.3 reflects no significant loss up to  $450\text{ °C}$  and no residue after  $650\text{ °C}$ . This confirms the purity of the PECNTs. The TGA curve of PECNTs/S shows major weight loss at  $150\text{ °C}$  to  $320\text{ °C}$  due to decomposition of sulfur, which confirms the sulfur weight percentage is approximately 83%.

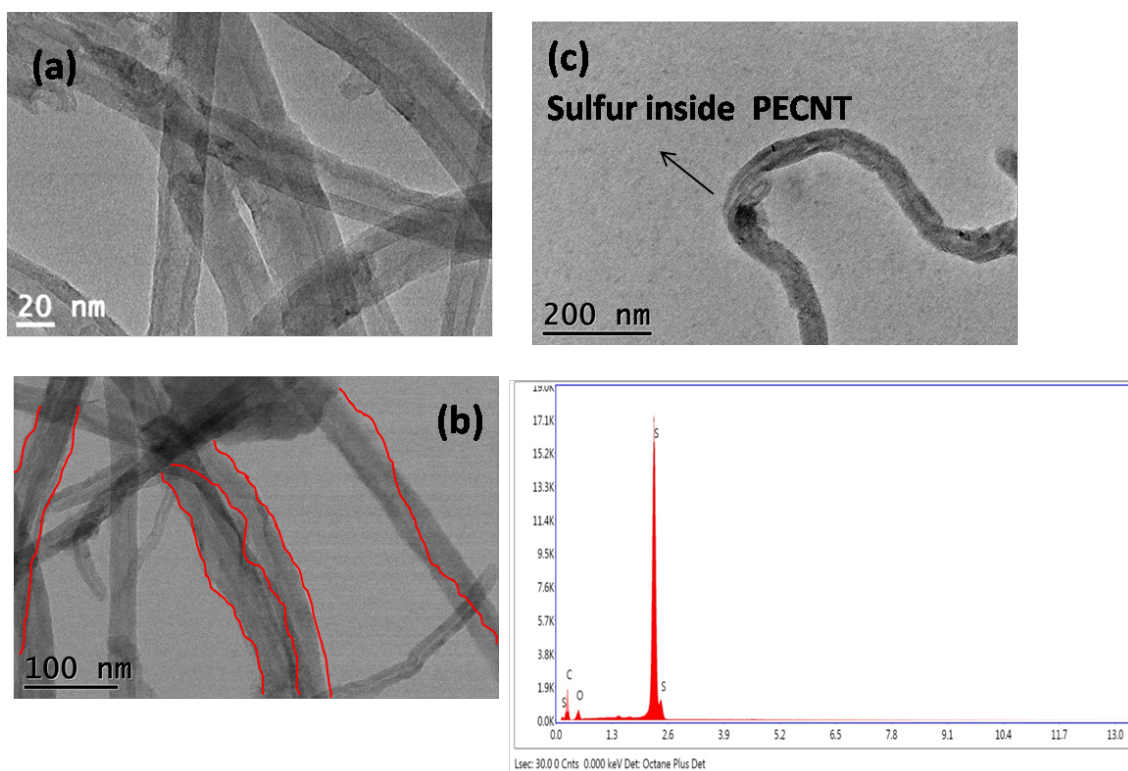
The morphological studies were carried out using TEM and shown in Fig.4. Fig.4 a) shows the randomly oriented carbon nanotubes. And fig (b) shows the unzipped outer layers can be seen in fig. 4(b) representing partially exfoliated carbon nanotube (PECNTs). Fig.5 shows the TEM image of randomly oriented sulfur incorporated PECNT (S@PECNTs). In Fig. 6(a) shows the TEM images of CNTs in which the inner core of carbon nanotubes is clearly visible which confirms the synthesized material as multi-walled carbon nanotubes. TEM images of PECNTs in Fig. 6(b) clearly demonstrate that few outer layers are exfoliated upon hydrogen exfoliation without disturbing the inner core of CNTs and it confirms PECNTs are the combination of 1D and 2D nanostructures of graphene ribbons and CNTs. Sulfur incorporated in PECNTs is clearly visible from Fig. 6(c). EDS spectrum of PECNTs confirms the presence of carbon, oxygen, and sulfur as shown in Fig. 6(d).



**Fig.4. TEM images of a) Randomly oriented carbon nanotubes.; (b) The unzipped outer layers can be seen in (b) representing partially exfoliated carbon nanotube (PECNTs).**



**Fig.5. TEM image of randomly oriented sulfur incorporated PECNT (S@PECNT)**



**Fig.6. TEM images of (a) CNTs (b) PECNTs (c) PECNTs/S (d) EDS of PECNTs/S**



### **Electrochemical measurements**

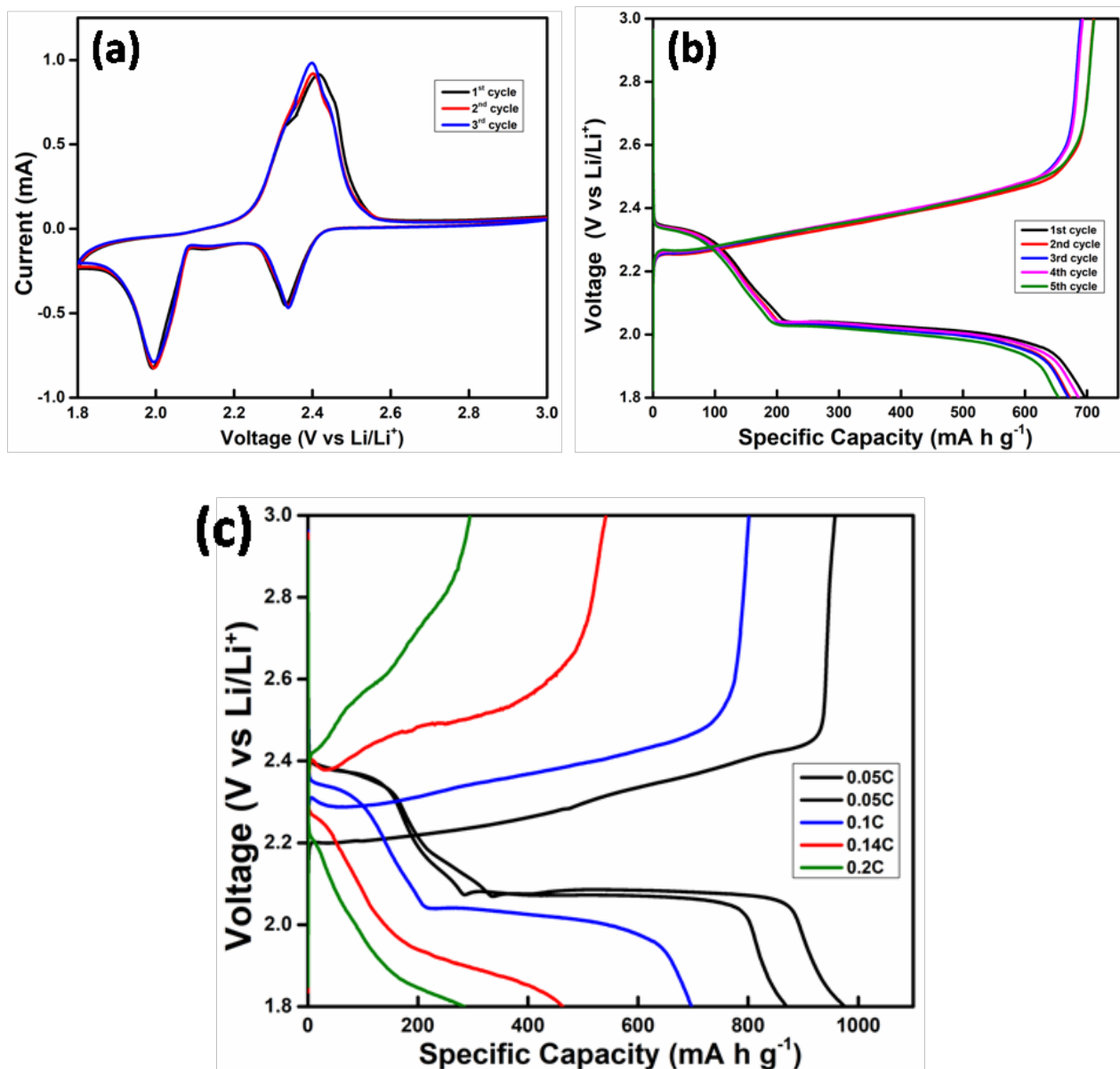
The working electrode was prepared by taking 75% of active material, 10 % acetylene black and 15 % PVDF binder mixed with NMP solvent. The prepared slurry was coated on an aluminum foil by doctor blade technique and dried overnight at 80 °C in vacuum oven. The dried sample was cut into 12 mm electrode disks. The 2032 coin assembly has been done in the argon-filled glove box by maintaining water and oxygen levels less than 0.1 ppm. The prepared PECNTs/S as a cathode, polypropylene as a separator, hydrophobic-PTFE coated carbon fabric with Li foil as anode. The coin cell assemblies are made with and without hydrophobic-PTFE coated carbon fabric. The electrolyte used was 0.1 M bis(trifluoromethane)sulfonimide lithium salt (LITFSI) in 1:1 ratio of 1,3-dioxolane (DOL) and dimethoxyethane (DME) with 0.2 M  $\text{LiNO}_3$  as additive.

### **Cyclic voltammetry measurement**

The cyclic voltammetry (CV) measurement is performed for the cells without and with hydrophobic-PTFE coated carbon fabric in the potential window 3.0 – 1.8 V. The two reduction peaks in CV represent the formation of higher order ( $\text{Li}_2\text{S}_8$ -  $\text{Li}_2\text{S}_4$ ) and lower order ( $\text{Li}_2\text{S}_2$ -  $\text{Li}_2\text{S}$ ) polysulfides and oxidation peaks indicate the oxidation of polysulfides and formation of sulfur.

### **Galvanostatic charge-discharge measurement**

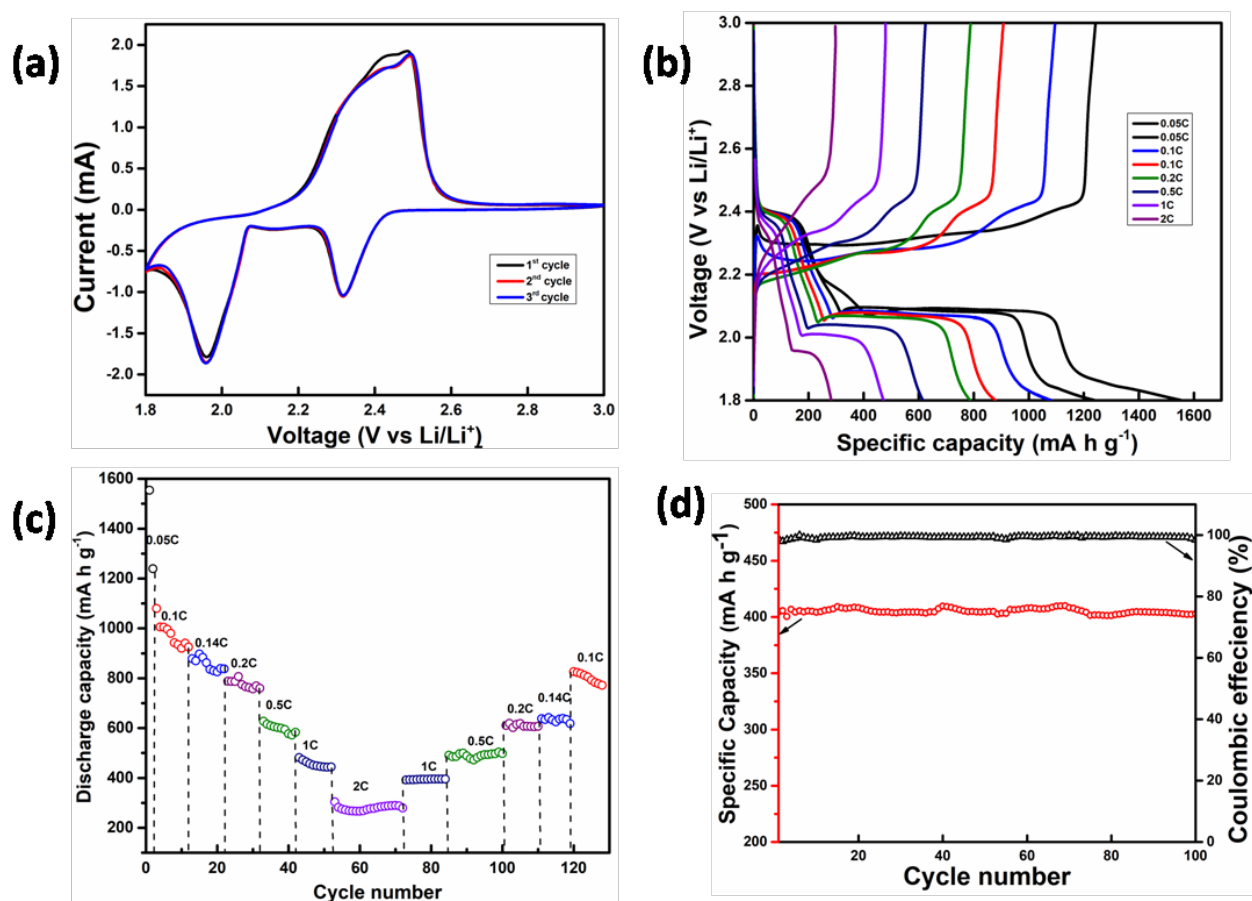
Galvanostatic charge-discharge is performed for the cells without and with hydrophobic-PTFE coated carbon fabric in the potential window 3.0 – 1.8 V at 0.1 C to 2 C ( $1\text{C} = 1672 \text{ mA g}^{-1}$ ). The cells without hydrophobic-PTFE coated carbon fabric have shown very less specific capacity and more fading. The hydrophobic-PTFE coated carbon fabric has shown better specific capacity and stability than the cells without hydrophobic-PTFE coated carbon fabric. This is mainly of two reasons, (i) the high surface area acts as polysulfide blockage minimizing the shuttle effect, (ii) the higher order polysulfides are hydrophilic, and the PTFE coated carbon fabric is hydrophobic. The higher order polysulfides when it reaches the hydrophobic-PTFE coated carbon fabric because its hydrophobicity bounces back to the cathode without reaching the anode. The synergistic effect of large surface area of PECNTs and hydrophobic PTFE carbon fabric has improved the specific capacity, rate capability, and stability of PECNTs/S cathode.



**Fig.7. (a) Cyclic voltammogram of PECNTs/S without hydrophobic-PTFE coated carbon fabric in the potential window 3.0-1.8V (b) Galvanostatic charge-discharge profiles of PECNTs/S without hydrophobic-PTFE coated carbon fabric at 0.1C (c) Galvanostatic charge-discharge profiles of PECNTs/S without i hydrophobic-PTFE coated carbon fabric at different C-rates**

Fig. 7(a) shows the cyclic voltammograms of PECNTs/S without hydrophobic-PTFE coated carbon fabric in potential window 3.0 -1.8 V. Fig. 7(b) represents the charge-discharge profile of PECNTs/S cathode without hydrophobic-PTFE coated carbon fabric at 0.1 C,

overcharging has taken place with the initial capacity is  $697 \text{ mA h g}^{-1}$ . The overcharging is clearly visible from a 5<sup>th</sup> cycle which has a discharge capacity of  $654 \text{ mA h g}^{-1}$  and corresponding charging capacity is  $711 \text{ mA h g}^{-1}$ . This overcharging has occurred due to shuttling of polysulfides from the cathode to the anode and oxidizing at the anode. Fig.7(c) replicates the galvanostatic charge-discharge curves at 0.05, 0.1, 0.14, 0.2 C. The higher order polysulfides reduction plateau at 0.05C - 2.36 V, 0.1C -2.33 V, 0.14C- 2.25V and 0.2C- 2.2V. As the C-rate increasing the higher order polysulfide plateau potential decreases and 0.2C is no significant plateau. This shows that the polysulfides have already migrated towards the lithium anode.



**Fig.8 PECNTs/S cathode with hydrophobic-PTFE coated carbon fabric-Li foil (a) Cyclic voltammogram in the potential window 3.0-1.8 V at scan rate  $0.1 \text{ mV s}^{-1}$  (b) Galvanostatic charge-discharge profiles at different C-rates (c) Rate capability (d) Cycling performance and coulombic efficiency at 1C.**

Fig. 8(a) shows the cyclic voltammogram of PECNTs/S cathode with hydrophobic-PTFE

coated carbon fabric-Li foil as anode. In the first cycle the reduction peaks at 2.316 V and 1.96 V corresponds to the reduction of sulfur to polysulfides and in second and third cycle reduction peak shifts overlaps with the first cycle signifies the stable formation of polysulfides due to effect of hydrophobic-PTFE carbon fabric which minimize the polysulfide shuttling and rearrangement of active sulfur from its original position to most stable positions with lowering the resistance<sup>4</sup>. Fig. 8(b) demonstrates the galvanostatic charge-discharge profile of PECNTs/S with hydrophobic-PTFE coated carbon fabric. The cell shows very high initial discharge capacity of  $1556 \text{ mA h g}^{-1}$  at 0.05 C due to formation SEI layer formation at cathode along with hydrophobic-PTFE coated carbon fabric. The second discharge at 0.05 C is  $1223 \text{ mA h g}^{-1}$  and at 0.1 C the discharge capacity is  $1080 \text{ mA h g}^{-1}$ , which is higher than the PECNTs/S cathode without hydrophobic-PTFE coated carbon fabric ( $697 \text{ mA h g}^{-1}$ ). This shows the hydrophobic-PTFE carbon fabric helps in trapping the polysulfides within the hydrophobic-PTFE coated carbon fabric and not moving towards the anode. The PECNTs/S with hydrophobic-PTFE coated carbon fabric-Li foil have showed the high rate capability up to 2C as shown in Fig. 8(c), after running cell at high current and going back to lower 0.1C the cell shows the specific capacity of  $767 \text{ mA h g}^{-1}$  after 10 cycles which can retain approximately 82 % of its initial capacity. Fig. 8(d) represents the cycling performance of the PECNTs/S with hydrophobic-PTFE coated carbon fabric-Li foil; this shows excellent cycling stability up to 100 cycles with 99.98% coulombic efficiency.

## Main conclusions

1. For PECNTs/S cathode and Li foil coupled with the hydrophobic coating on PTFE carbon fabric as anode, the discharge at 0.05 C is  $1223 \text{ mA h g}^{-1}$  and at 0.1 C the discharge capacity is  $1080 \text{ mA h g}^{-1}$ , which is higher than the PECNTs/S cathode without hydrophobic coating ( $697 \text{ mA h g}^{-1}$ ). **Thus the hydrophobic coating-PTFE carbon fabric helps in trapping the polysulfides and does not allow towards the anode.**
2. PECNTs/S cathode with Li foil coupled with the **hydrophobic coating on PTFE carbon fabric as anode shows a high rate capability up to 2C**. And after running cell at high current and reverse back to lower 0.1 C, the cell shows a specific capacity of  $767 \text{ mA h g}^{-1}$  after 10 cycles which can retain approximately 82 % of its initial capacity.

3. *PECNTs/S cathode with Li foil coupled with the hydrophobic coating on PTFE carbon fabric as anode shows an **excellent cycling stability up to 100 cycles** with 99.98% coulombic efficiency.*
4. *PECNTs/S cathode with Li foil coupled with the hydrophobic coating on PTFE carbon fabric as anode **shows an improved sulphur utilization, rate capability and cyclic stability.***

## Output

1. *An Efficient hydrophobic coating on PTFE carbon fabric for Polysulfide Blockade for Improved Performance of Lithium Sulfur Battery, manuscript under preparation (2017).*
2. *Methods to Block Polysulfide for Improved Performance of Lithium Sulfur Battery, invention under preparation (2017).*

## References:

- 1 a. L. M. Reddy, M. M. Shaijumon, N. Rajalakshmi and S. Ramaprabhu, *J. Fuel Cell Sci. Technol.*, 2010, **7**, 21001.
- 2 P. Tamilarasan and S. Ramaprabhu, *J. Mater. Chem. A Mater. energy Sustain.*, 2014, **2**, 14054–14063.
- 3 S. Ghosh and S. Ramaprabhu, *J. CO2 Util.*, 2017, **21**, 89–99.
- 4 Yu-Sheng Su and A. Manthiram, “A new approach to improve cycle performance of rechargeable lithium–sulfur batteries by inserting a free-standing MWCNT,” *Chem. Commun.*, vol. 48, July 2012, pp. 8817–8819